



Progress Status of Skutterudite-Based Segmented Thermoelectric Technology Development

21st Symposium on Space Nuclear Power and Propulsion

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Acknowledgements:

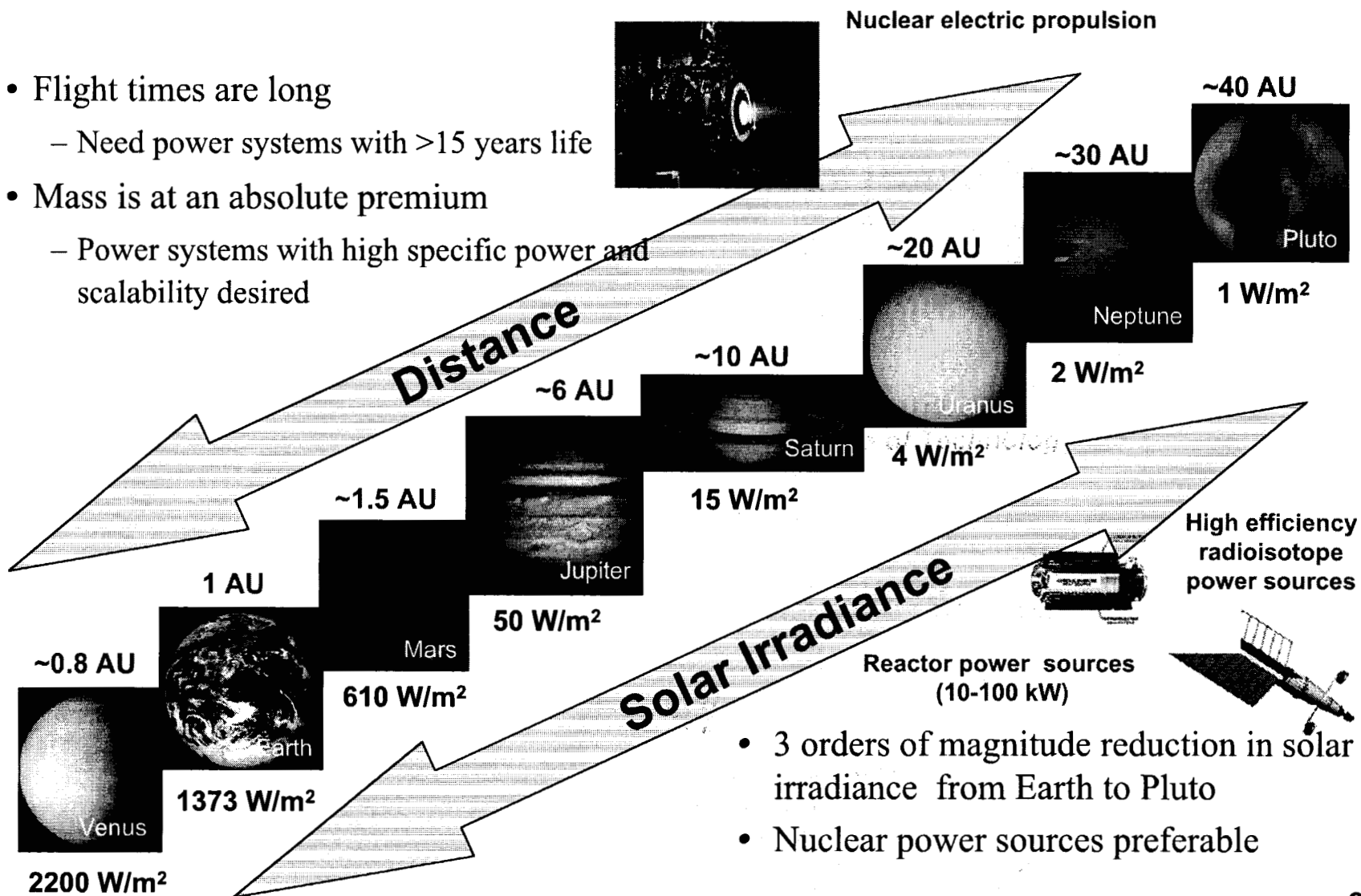
Prof. M. El-Genk (University of New Mexico)

NASA, ONR & DARPA



Power Technology

- Flight times are long
 - Need power systems with >15 years life
- Mass is at an absolute premium
 - Power systems with high specific power and scalability desired





Advanced Radioisotope Power Systems (APRS) **for NASA missions**

- **Overall objective**

Develop low mass, high efficiency, low-cost Advanced Radioisotope Power System with double the Specific Power and Efficiency over state-of-the-art radioisotope thermoelectric generators R(TGs)



TASK Overview



Technology Description

- Direct thermoelectric energy conversion device
- Employs segmented unicouples and advanced TE materials to achieve higher efficiency

Program Objectives

- Develop Segmented Thermoelectric (STE) Converter technology with a projected 975K-375K efficiency of 12.5%
- Transfer technology to industry/DOE for integration into a radioisotope power system that can provide a specific power of ~7-8 W_e/kg and ~10% efficiency
- Develop high efficiency 1275K-975K TE materials and unicouples with a goal of 15-17% converter efficiency

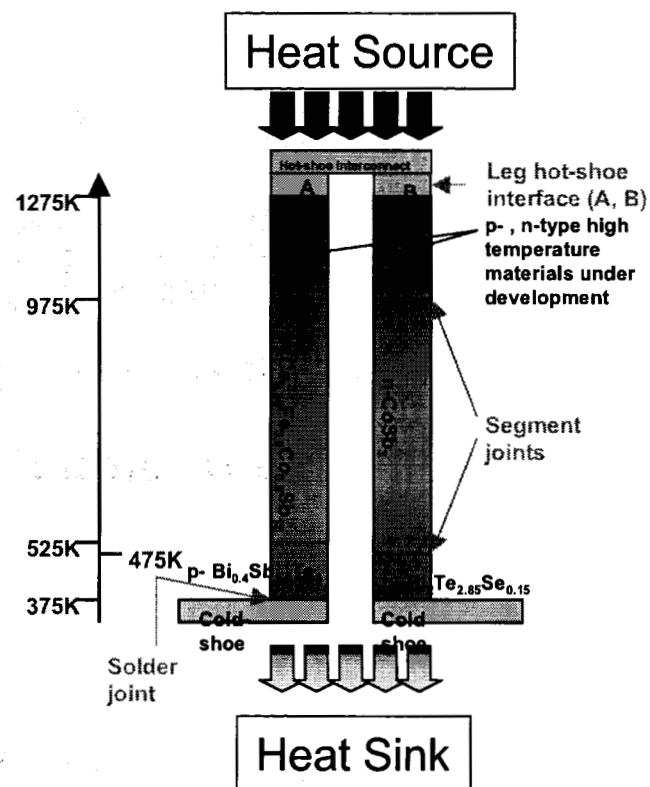


Illustration of advanced segmented unicouple

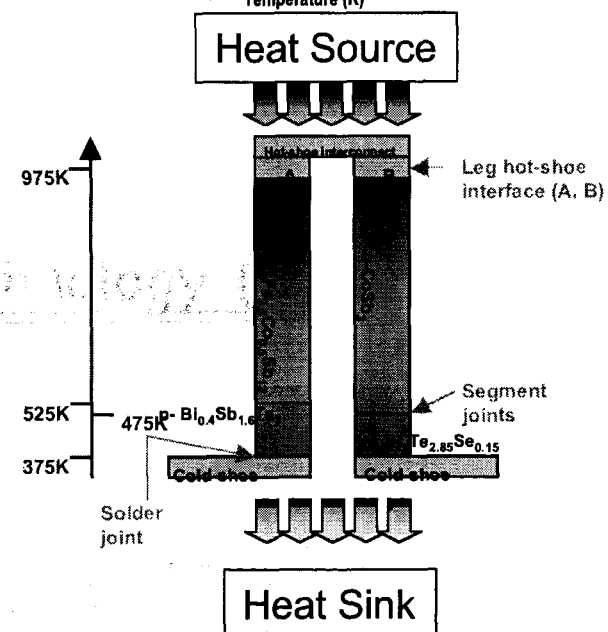
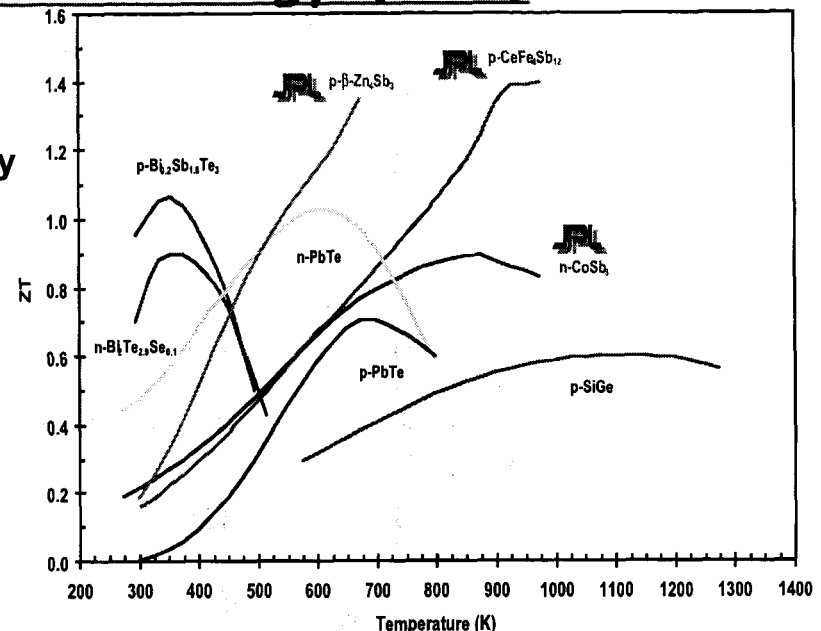


Segmented Thermoelectric Technology (STE)



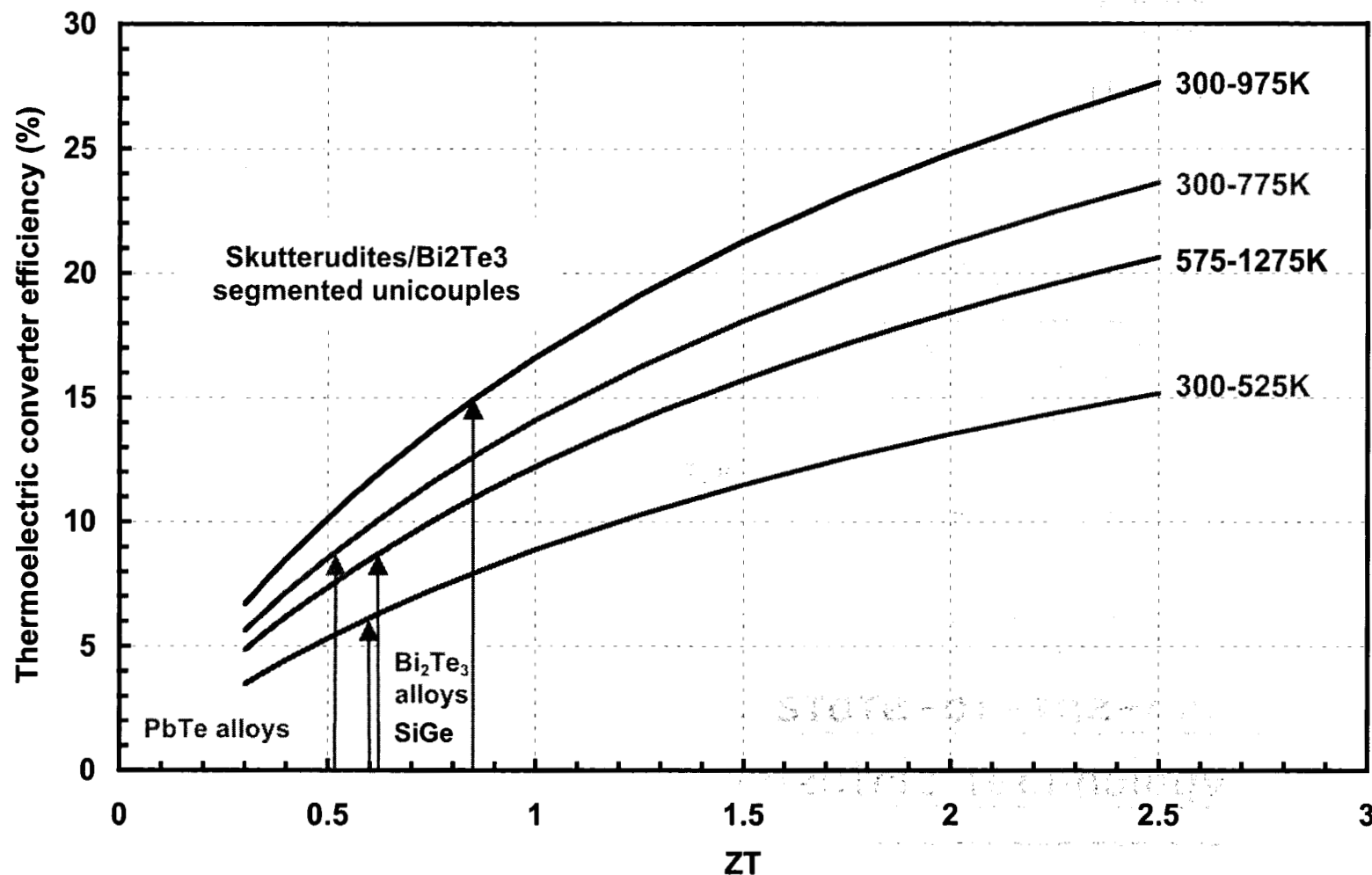
- **New high ZT materials ZT**
 - Development initiated in 1991 and supported by ONR and DARPA
 - Higher efficiency values
- **Segmented uncouples**
 - Large ΔT , high ZT \rightarrow high efficiency
 - Using a combination of state-of-the-art TE materials (Bi_2Te_3 -based materials) and new, high ZT materials developed at JPL
 - Skutterudites : $\text{CeFe}_4\text{Sb}_{12}$ and CoSb_3
 - Zn_4Sb_3
 - Current materials operation limited to $\sim 975\text{K}$
 - Higher average ZT values
 - ➔ Higher material conversion efficiency
 - ➔ Up to 15 % for a 300-975K temperature gradient

$$\text{Efficiency } \eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$





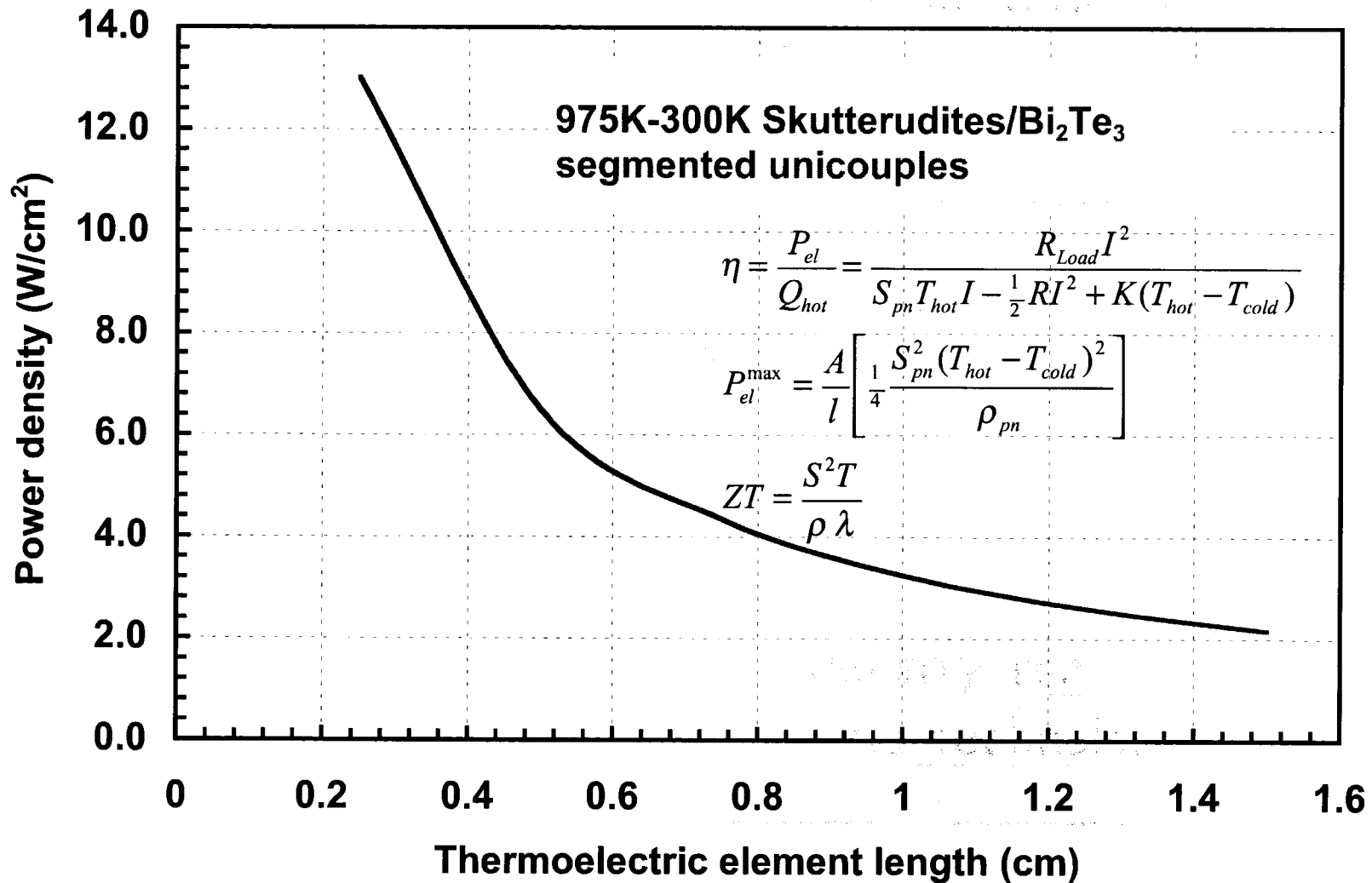
Converter efficiency : state-of-the-art vs. segmented thermoelectric technology



STE technology has the potential for achieving twice the converter efficiency of SOA thermoelectrics



Calculated power density for segmented thermoelectric technology

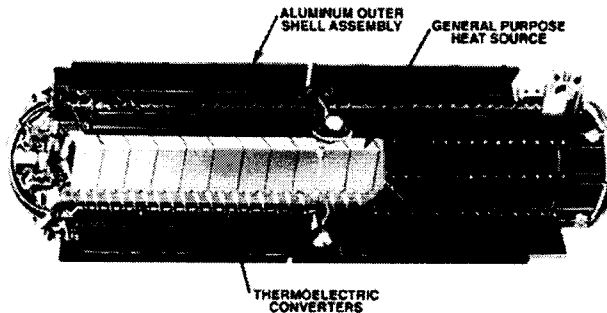




General Purpose Heat Source RTG

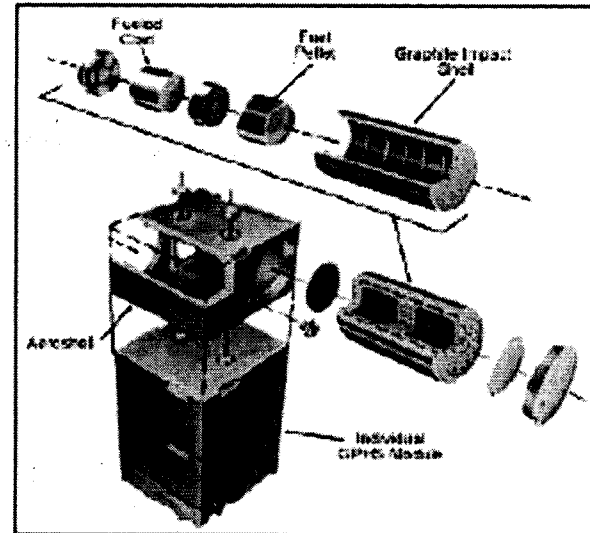


General Purpose Heat Source (GPHS) Radioisotope Thermoelectric Generator (RTG)

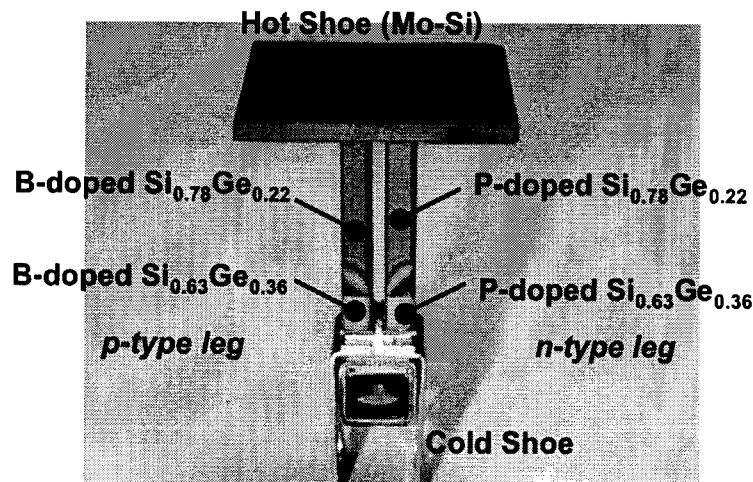


- POWER OUTPUT - 285 W(e)
- FUEL LOADING - 4400 W(t): 132,500 Ci
- WEIGHT - 124 lbs
- SIZE - 16.6 in x 44.5 in

The three Radioisotope Thermoelectric Generators (RTGs) provide electrical power for Cassini's instruments and computers. They are being provided by the U.S. Department of Energy.



General Purpose Heat Source Module



GPHS SiGe unicouple

GPHS-RTG Performance Data

Power output-We	290 beginning of life 250 end of life
Operational life - hrs	40,000 after launch
Weight-kg	55.5
Output voltage	28
Dimensions	42.2 diameter 114 long
Hot junction temperature-K	1270
Cold junction temperature-K	566
Fuel	PuO ₂
Thermoelectric material	SiGe
Numbers of unicouples	572
Mass of Pu-238-g	7,561



STE-ARPS

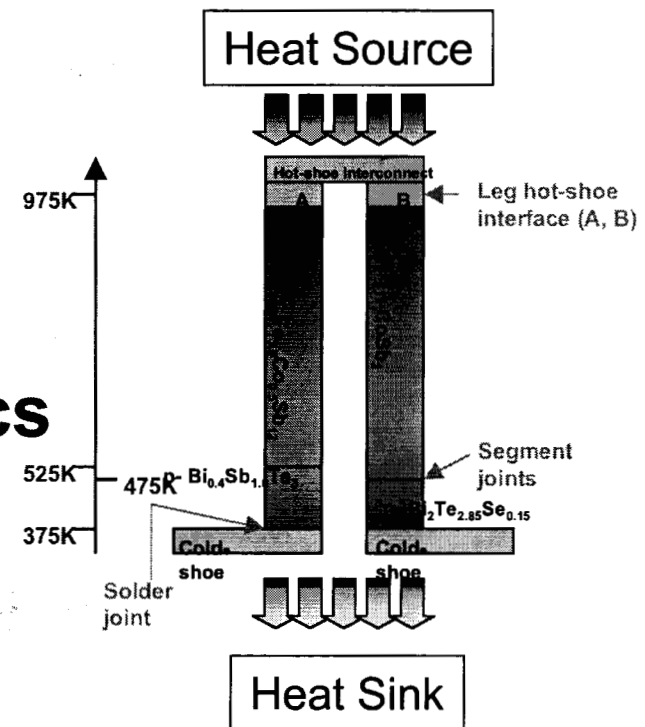


•STE-ARPS

- Would use advanced materials segmented legs
 - 700 to 100°C operation
 - Current GPHS-RTG unicouple design would be mostly conserved
 - Modifications required to radiator fins to accommodate for lower rejection temperature
 - Shorter housing
- New segmented unicouples could “replace” unicouples almost “one for one”

•Advantages of thermoelectrics

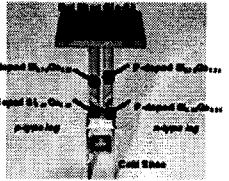
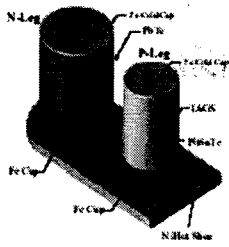
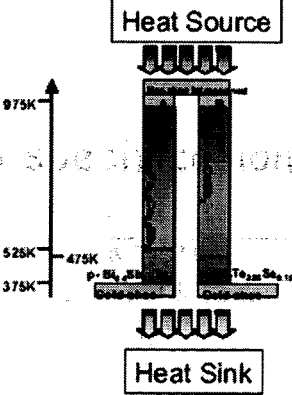
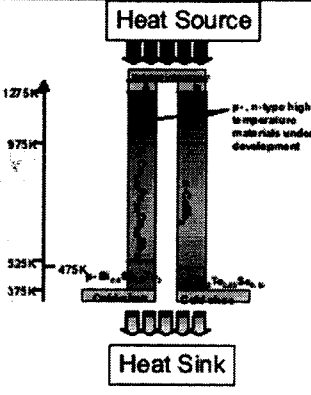
- Flight proven, long life demonstrated
- Solid state energy conversion -> reliability, no vibration, no moving parts
- Scalable
- No single point failure
- Significant system heritage





Projected STE 100W class ARPS specifications vs. SOA

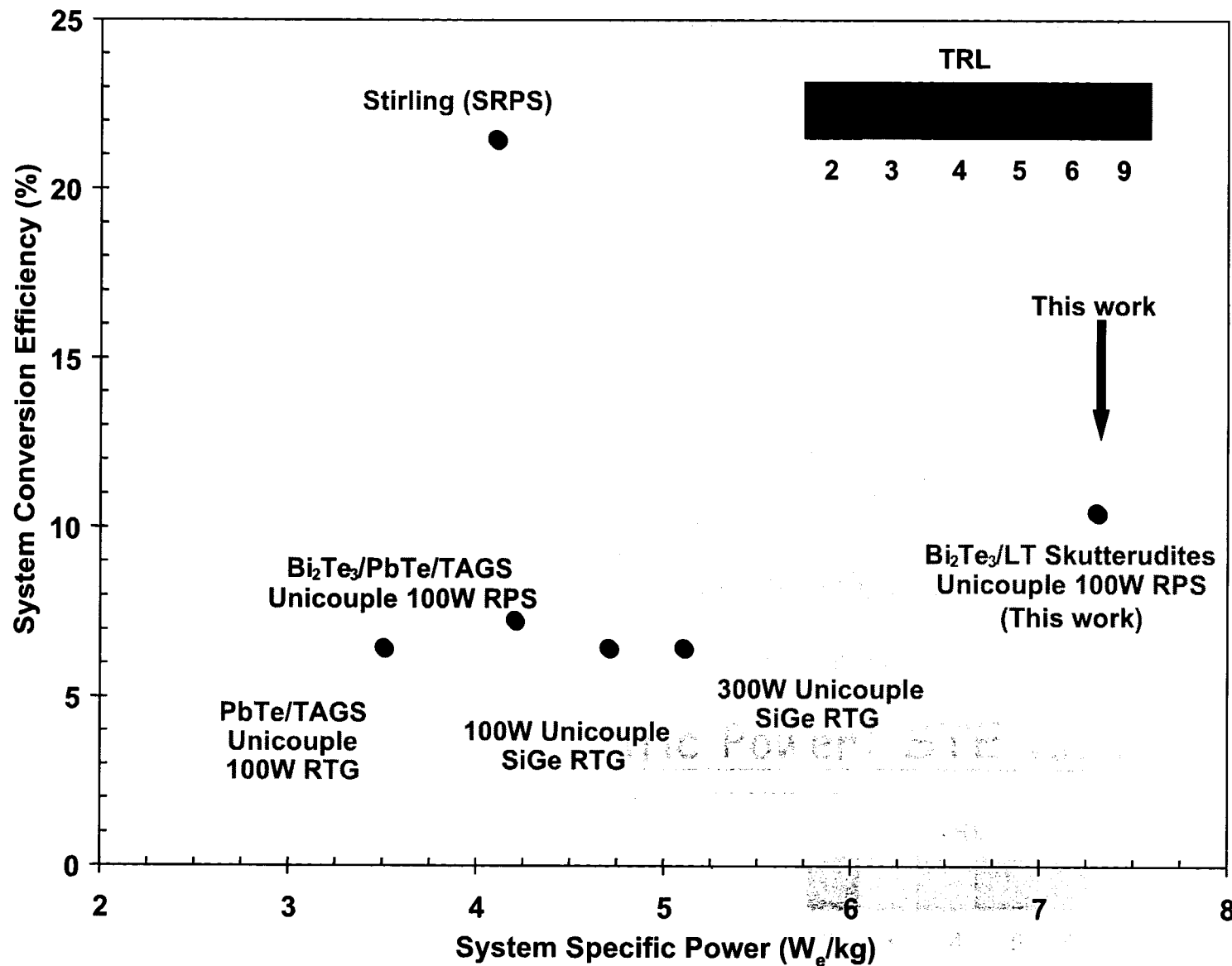


Item/Converter	SiGe-RTG	PbTe/TAGS MMRTG	Low T STE (LSTE)	High Temperature TE (HSTE)
Hot side temperature (K)	1273	823	975	1200
Cold side temperature (K)	573	453	375	375
Converter efficiency (%)	7.2	7.6	12.5	14.7
System efficiency (%)*	6.5	6.4	11.18	13.3
Thermal power (BOM)(W_{in})	2000	2000	1250	1000
Thermal efficiency (%)	85		85	85
Electrical power (BOM)(W_e)	107	110	118.8	113.0
Number of modules	8	8	5	4
Total PuO_2 mass (kg)	5.02	5.02	3.138	2.51
Total system mass estimate (kg)	23.24	38.1	16.3	13.1
- GPHs mass (kg)	11.54	12.83	7.215	5.77
- Housing (Kg)	3.1	4.2	1.90	1.55
- Radiator fins (kg)	0.45	3.32	1.7	1.36
- Converter (kg)	5.65	10	3.9	3.12
- Other structure (kg)	2.5	5.5	1.6	1.28
Specific power estimate (W_e/kg)	4.6	2.88	7.28	8.64
Unicouples				

* 90% of converter efficiency



System Efficiency & Specific Power: STE vs. SOA





Technology challenges

Task I : 975K-375K Unicouple Development

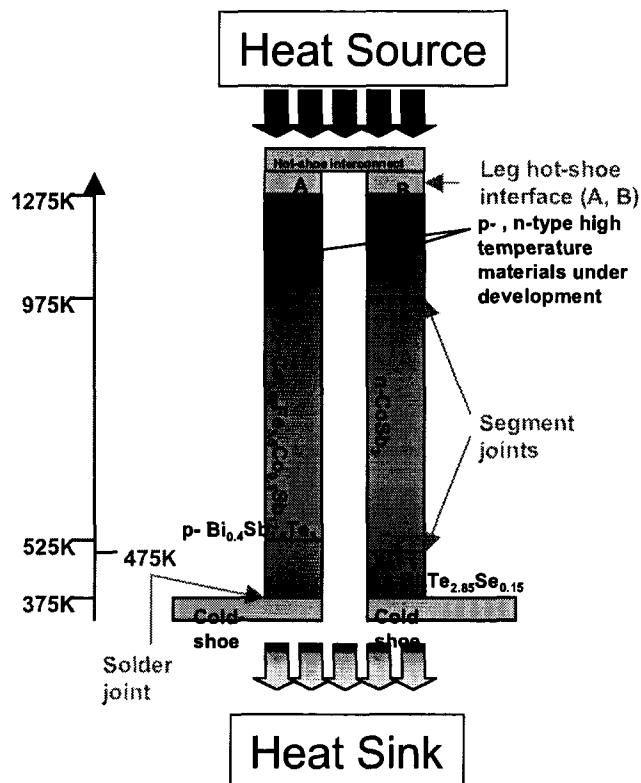
Key technology challenges

- TE materials processing and segmented leg fabrication
- Low electrical contact resistance between segments and between segments and cold- and hot-shoes
- Unicouple mechanical integrity
- Lifetime prediction model
 - Sublimation control
 - Stable thermoelectric properties
- Demonstrate unicouple performance
 - Testing and modeling

Task II : 1275K-975K High Temperature Materials Development

Key challenges

- Develop high ZT TE materials in 1275K-975K temperature range
- Demonstrate temperature stability for new materials
- Develop 1275K-975K segmented legs fabrication process





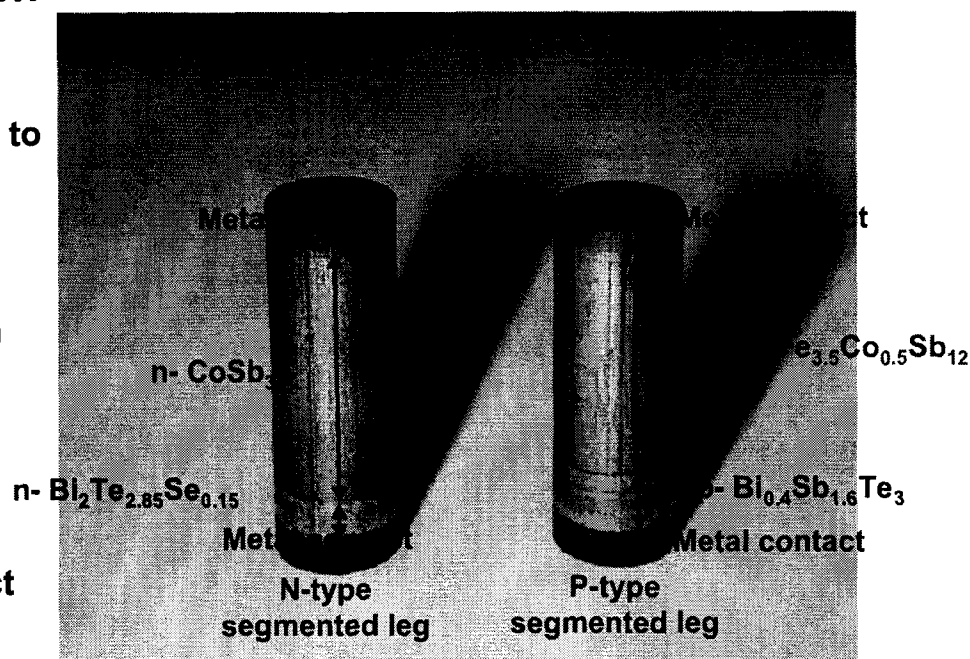
Segmented legs fabrication and characterization



Unicouples legs



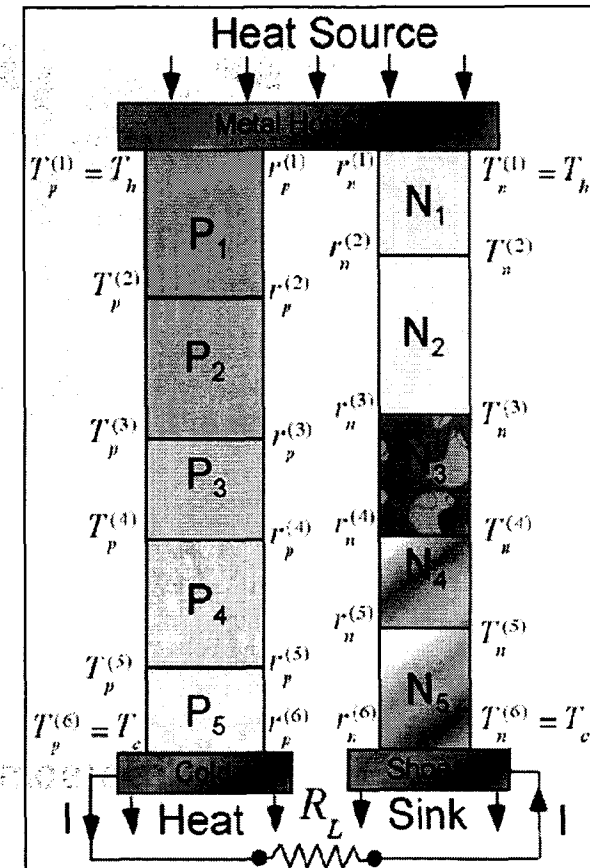
- **Uniaxial hot-pressing of powdered materials stacked on the top of each other**
 - Temperature optimized → density close to theoretical value
 - In graphite dies and argon atmosphere
 - With metallic diffusion barriers between the TE materials
 - Metallic contacts at hot- and cold-side
 - Low electrical resistance bonds ($<5\mu\Omega\text{cm}^2$) achieved → negligible impact on overall uncouple performance





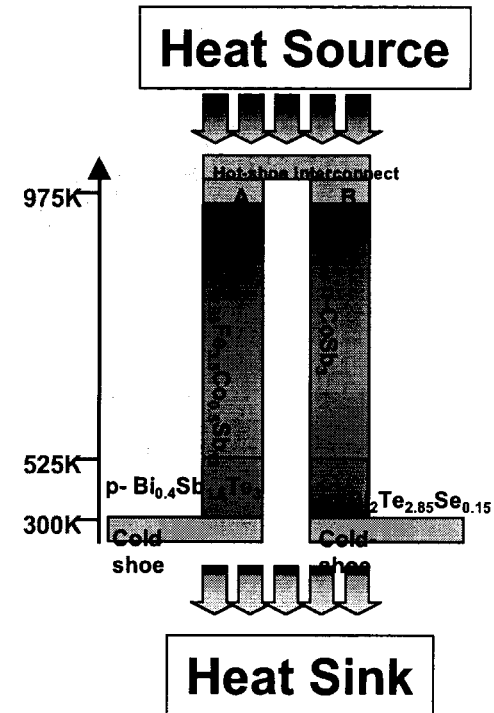
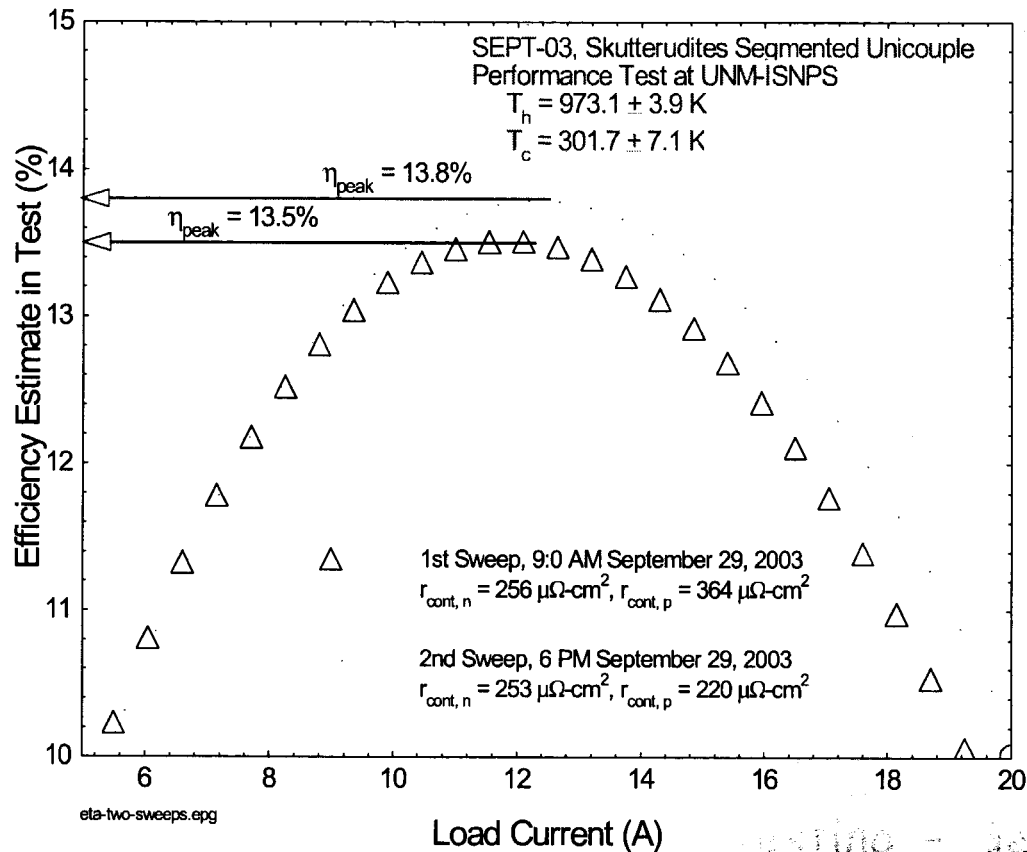
1-D Analytical Model of Segmented Thermoelectric Unicouples

- One-dimensional analytical model of STEs, with up to 5 segments per leg, is coupled to a *genetic algorithm* for maximizing either the electrical power or efficiency
- Input:
 - TE materials properties
 - Total length and composition of n- and p-legs
 - Cross sectional area of the p-leg (or the n-leg)
 - Hot and cold shoe temperatures
 - Total contact resistance per leg
- Output
 - Number of needed segments in n- and p-legs
 - Interface temperatures between various segments
 - Lengths of various segments in n- and p-legs
 - Cross sectional area of n-leg (or p-leg)
 - Electrical power and conversion efficiency curves
 - Operation I-V characteristics





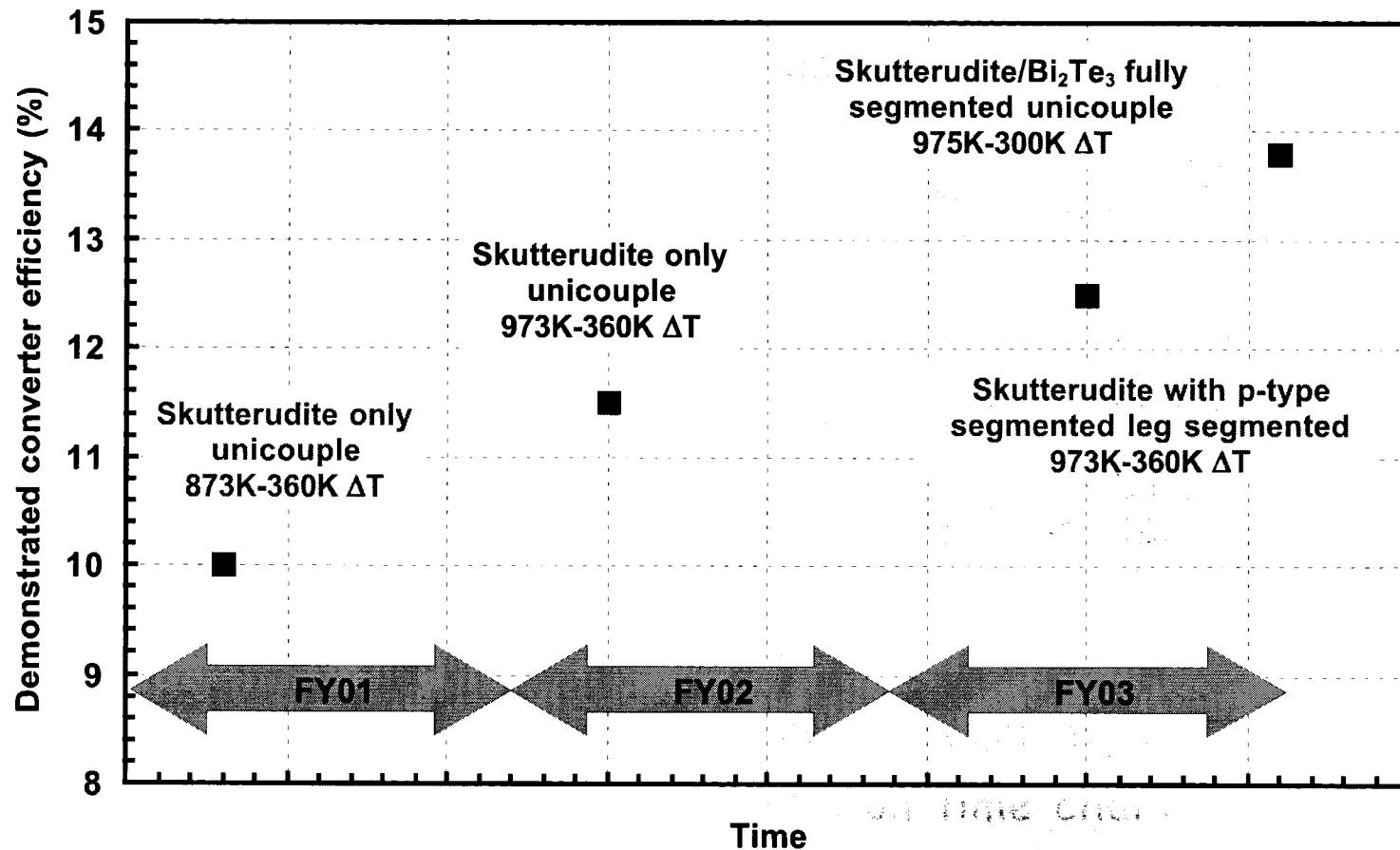
Thermal and electrical testing - Segmented unicouple



- Achieved 13.8% efficiency for 975K-300K ΔT
 - For fully segmented unicouple
- Fully validate projected performance



Efficiency demonstration time chart



- Latest results fully validate projected performance

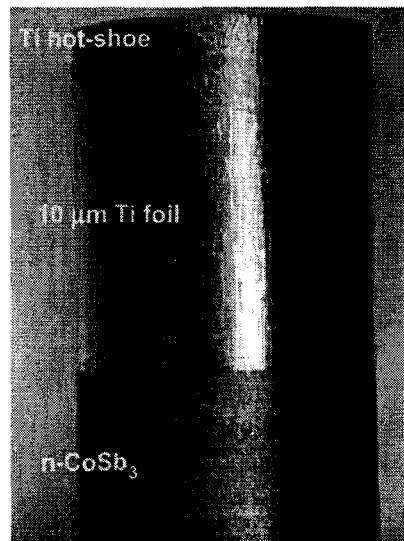


Lifetime & Sublimation studies

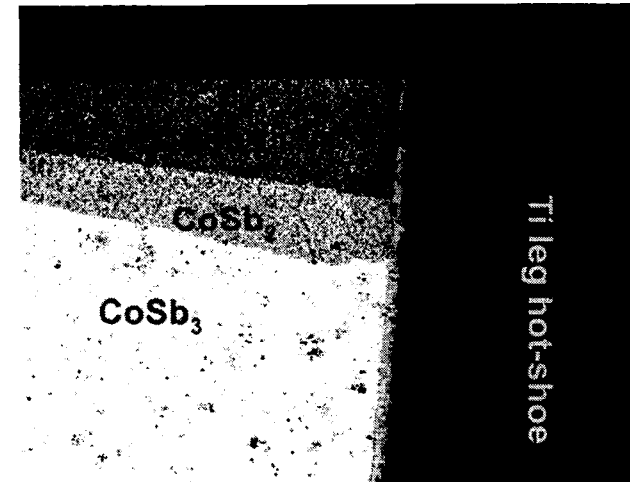


Sublimation control experiments

- **Uncoated samples**
 - Weight loss and temperature stability showed Sb sublimation in dynamic vacuum for T from ~ 875 to 975K for N-and p-type skutterudites
 - Decomposition into lower antimonide compounds
 - Appears to be diffusion limited



N-type Ti coated skutterudite leg



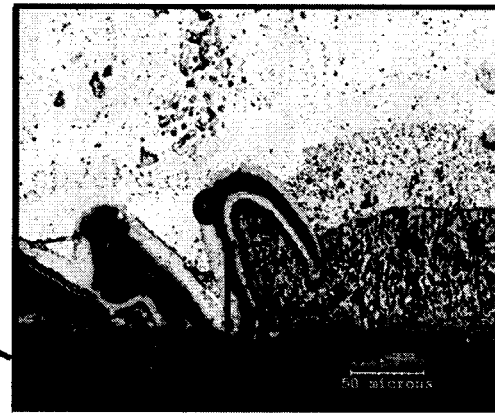
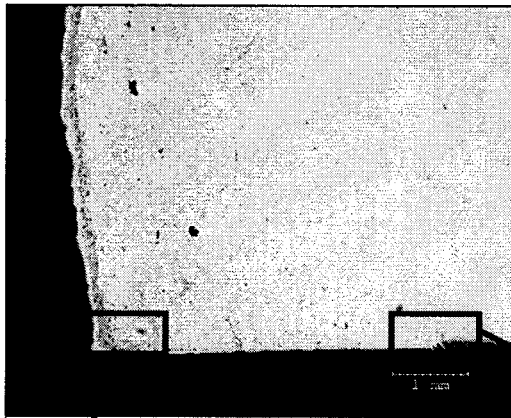
Photograph showing the decomposition of a CoSb₃ sample annealed at 875K for 3 months

- **Sb sublimation control studies**
 - Use of cover gas significantly suppresses Sb sublimation
 - ~ 10 μm metallic film applied during hot-pressing
 - Performed in gradient Ti film-coated leg life tests
- Thermal/mechanical modeling performed to evaluate impact on uncouple performance



Coated *n*-type tested in-gradient for 20 days

975K →

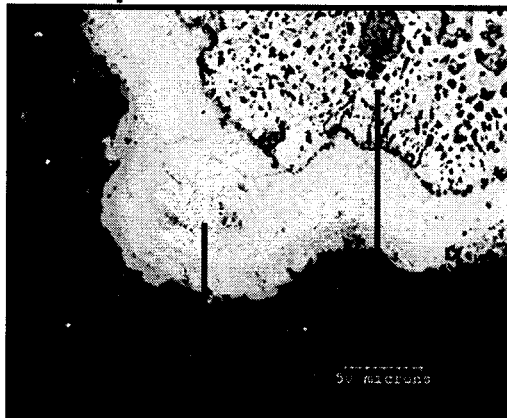


CoSb

CoSb

CoSb

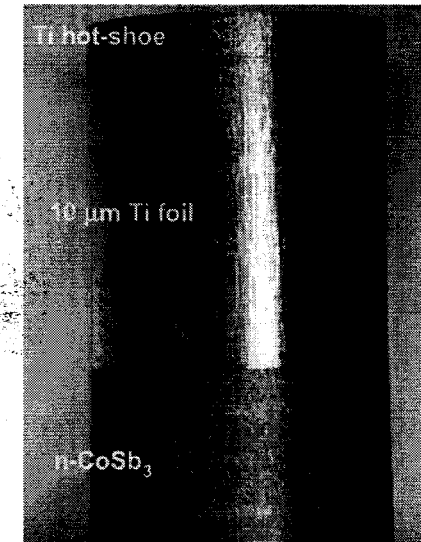
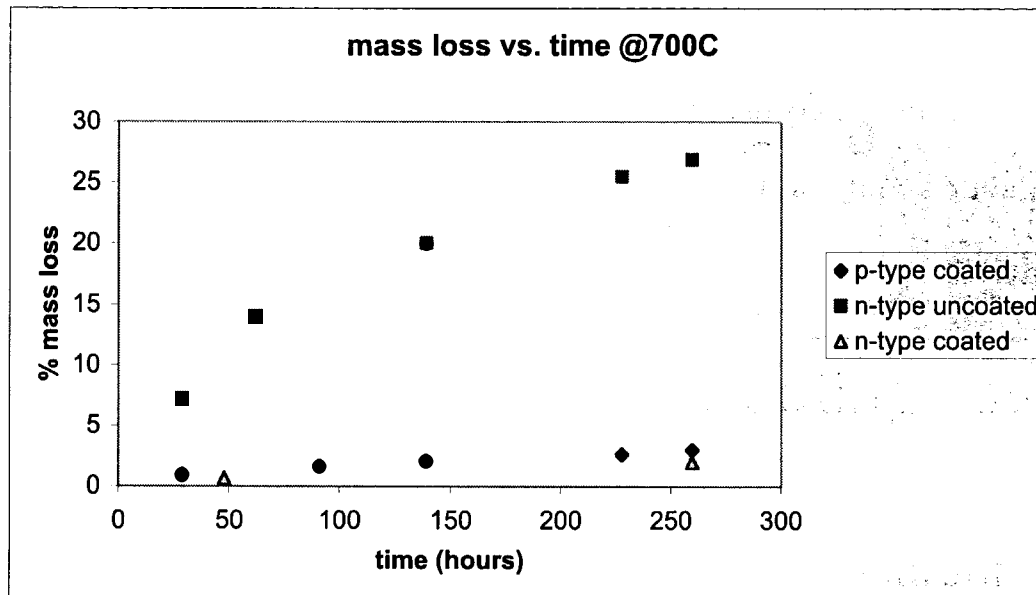
Coating stops



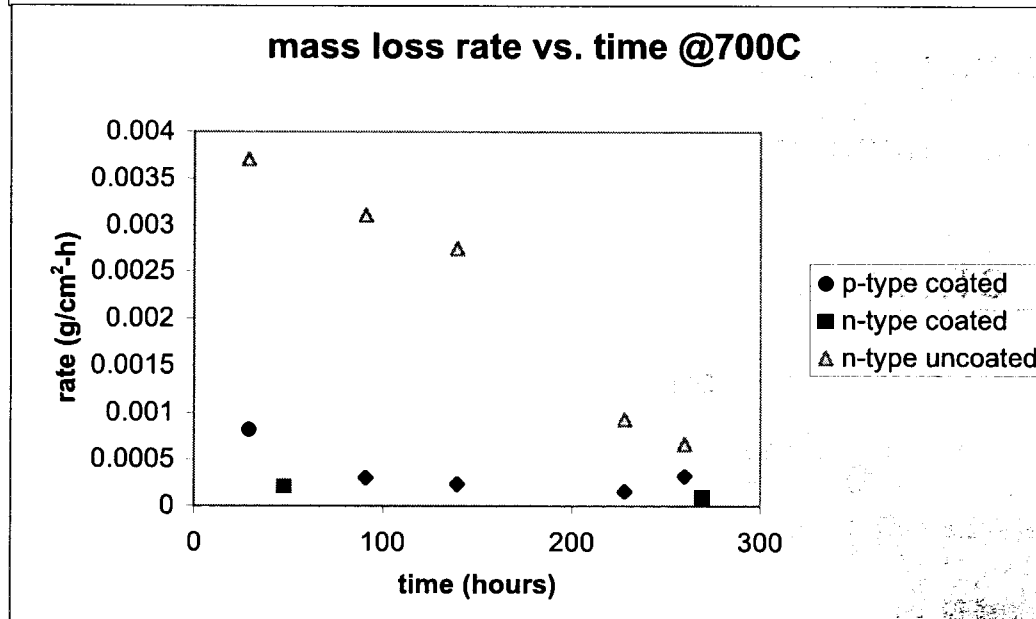
- No apparent degradation after 20 days
- Metal junction still intact
- Significant improvement over uncoated



Weight loss experiments results



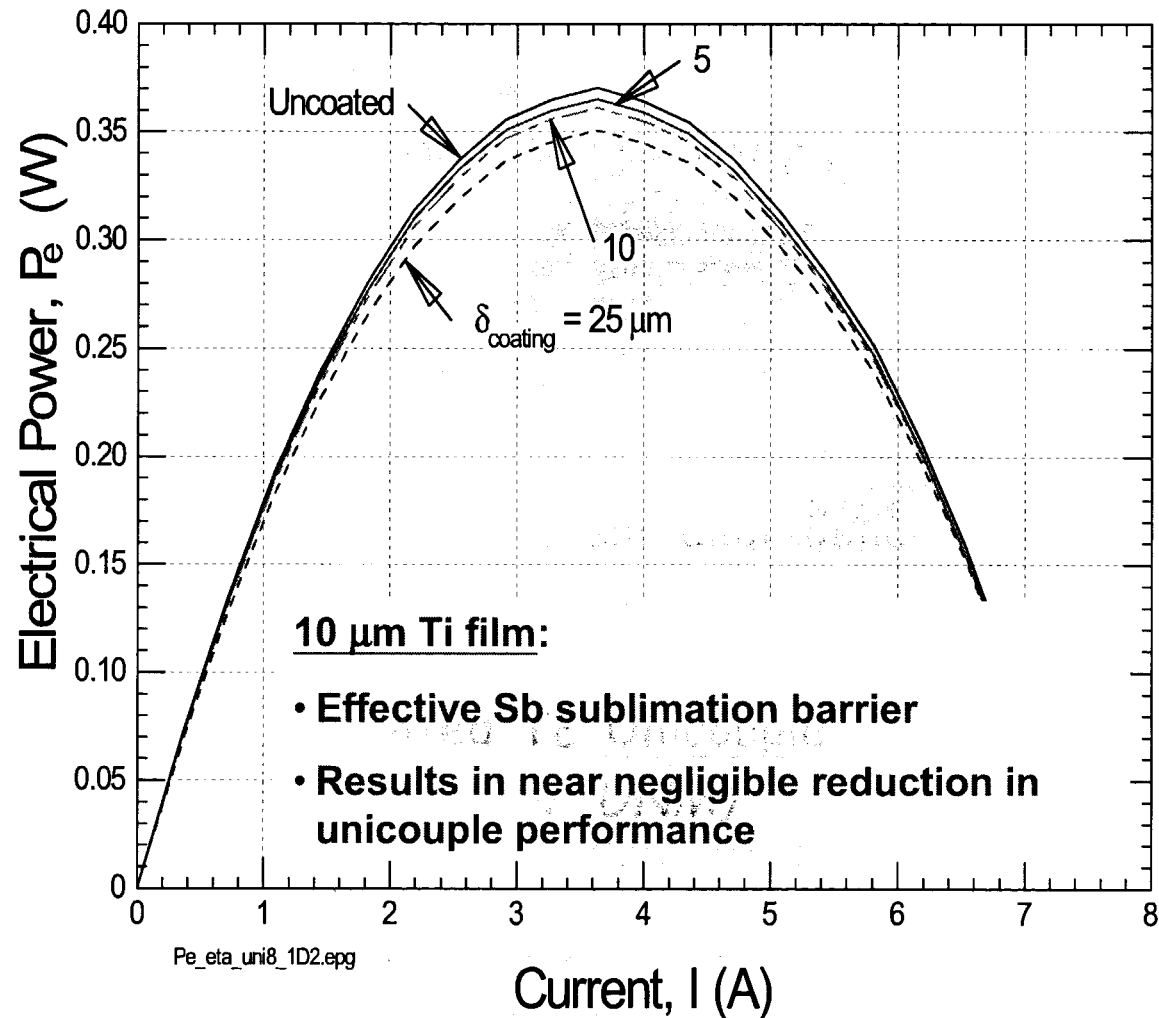
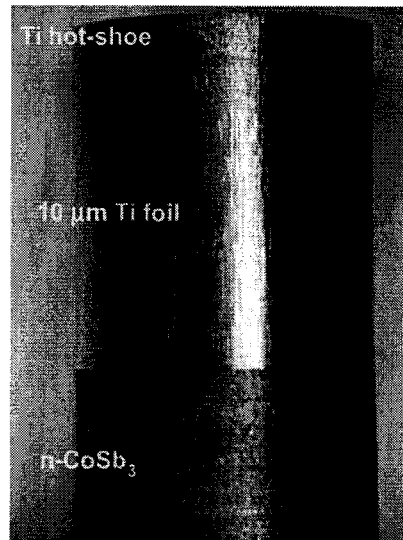
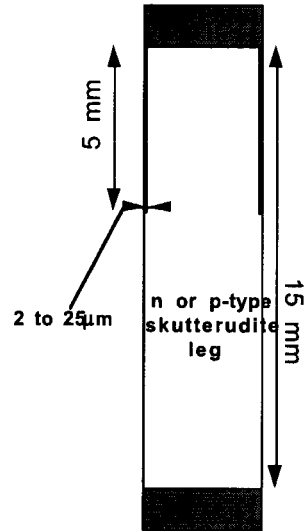
N-type Ti coated
skutterudite leg



- Ti coating results in a significant mass loss reduction over uncoated



975K-375K Segmented TE Unicouple performance modeling (UNM)



Coating Material: Ti (length 5 mm and thickness = 0-25 μm)



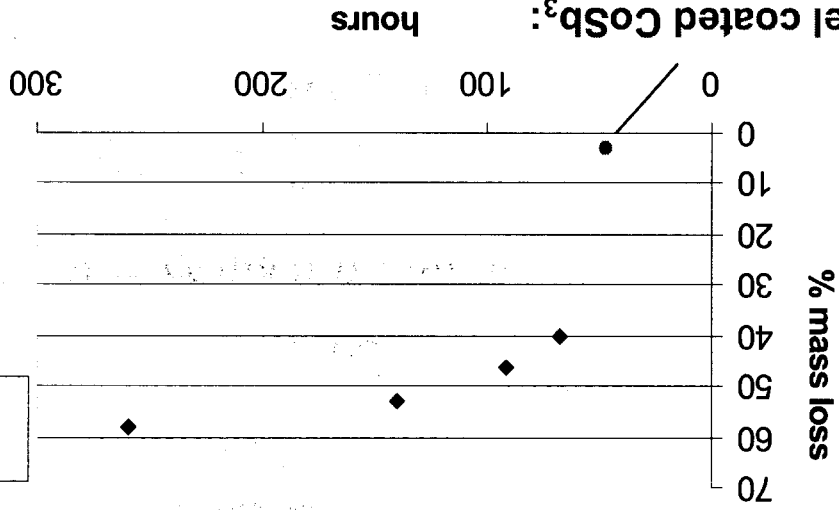
Aerogel encapsulated samples weight loss experiments



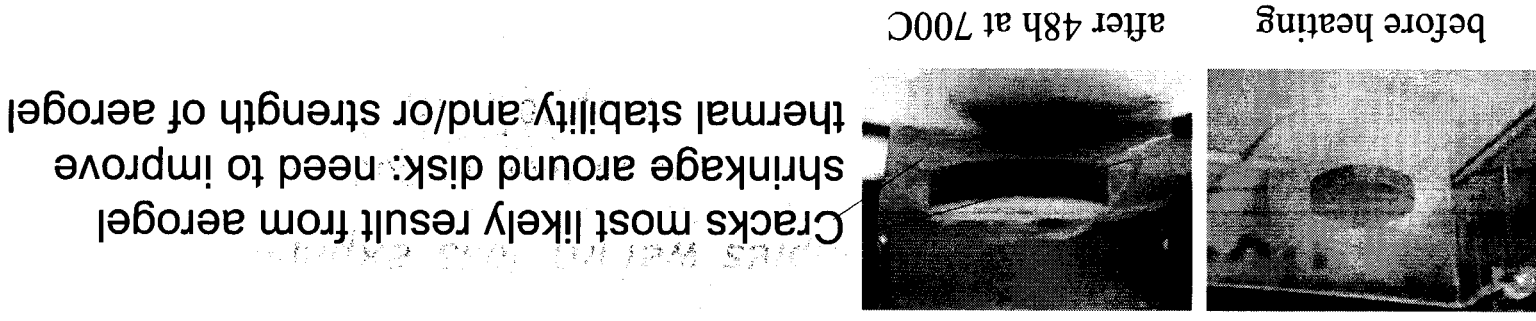
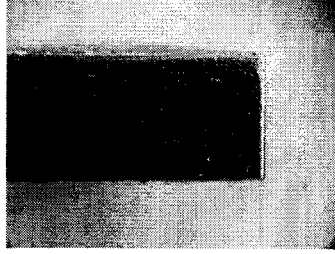
% mass loss vs. time for CoSb_3 disks

(700C 10^{-6} torr)

- aerogel coated disk
- ◆ uncoated disk



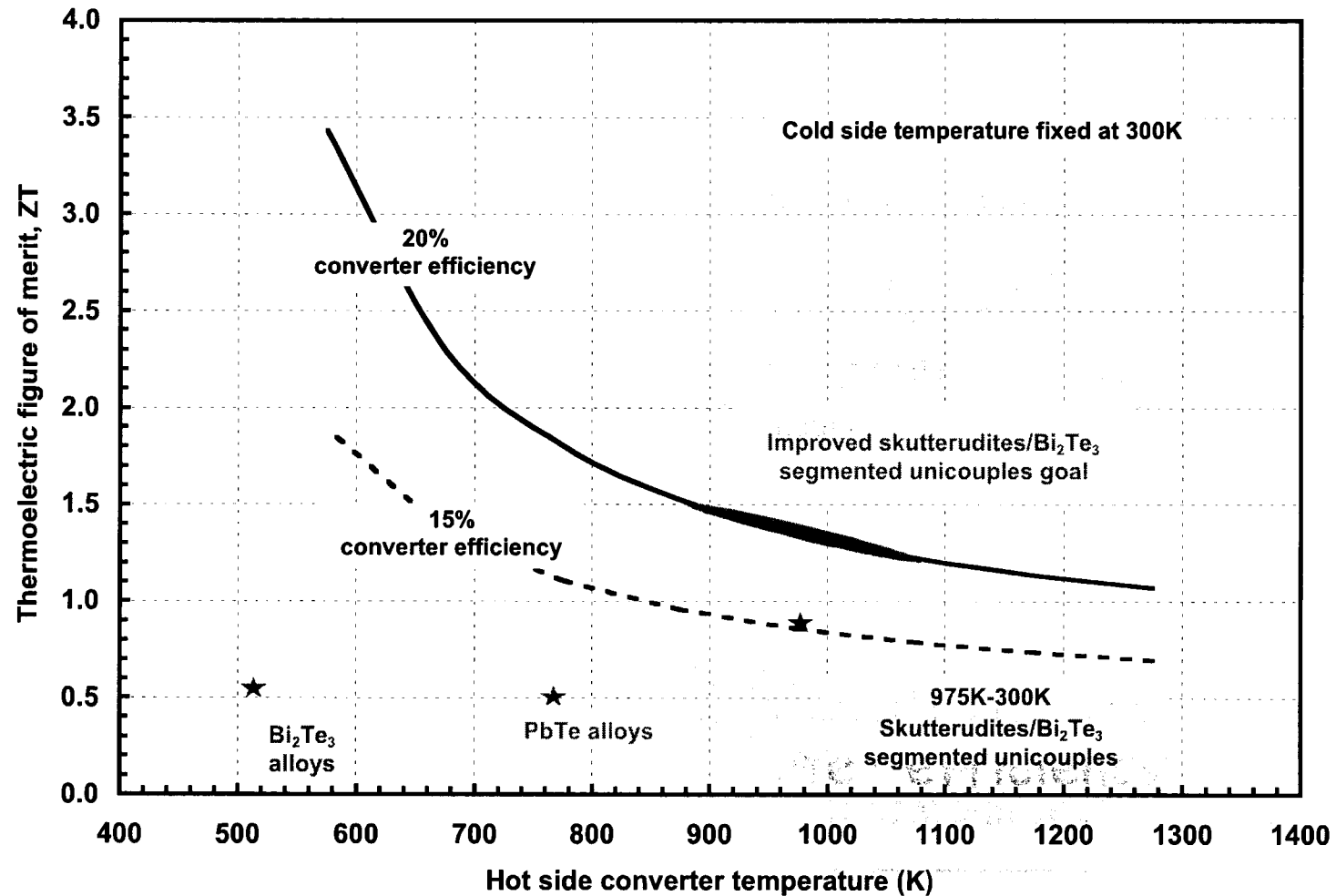
Aerogel coated CoSb_3 :
despite some cracks in
aerogel, no depletion
layer after 48h at 700C



Cracks most likely result from aerogel shrinkage around disk: need to improve thermal stability and/or strength of aerogel



Achieving 20% Converter efficiency





High-Temperature Materials

9/10/2011



Accomplishments - High Temperature Materials

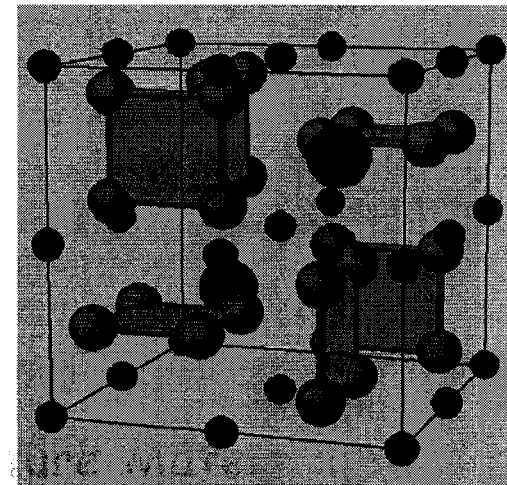


- **Phosphide and arsenide skutterudites; efforts were focused on five areas**

- **CeFe₄As₁₂ synthesis**
- **Synthesis of CoP₃ - NiP₃ solid solutions with 50% Ni**
- **Bulk CoP₃ synthesis**
- **Doped CoP₃**
- **Doping CoAs₃ - CoP₃ solid solutions**
- **Developed synthesis process, fabricated samples and measured key thermoelectric properties**

- **Skutterudite antimonides**

- **Demonstrated phase stability**
 - up to 1275K for IrSb₃ and CeRu₄Sb₁₂
 - up to 1175K for Ir rich Ir_{1-x}Co_xSb₃ solid solutions
- **Synthesized several heavily Pd/Pt doped samples with adjusted doping level based on microprobe measurements but ZT values remained relatively low**



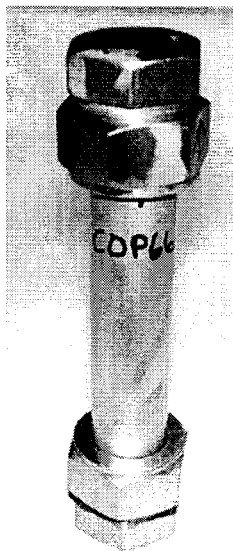
Skutterudite crystal structure



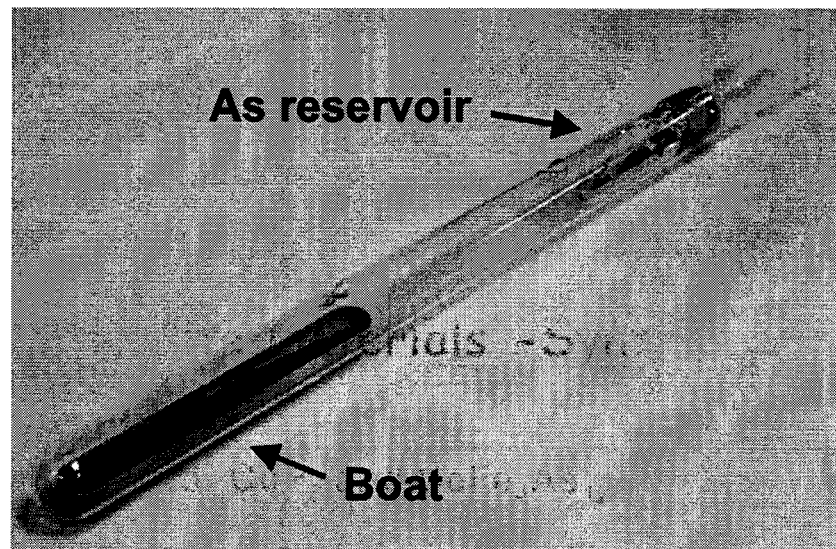
Phosphide and arsenide skutterudite materials - Synthesis

- Successfully developed synthesis process for CoP_3 and $\text{CeFe}_4\text{As}_{12}$ sample runs were completed

Steel ampoule developed for high pressure CoP_3 synthesis



Vapor transfer synthesis ampoule developed for As rich growth of $\text{CeFe}_4\text{As}_{12}$

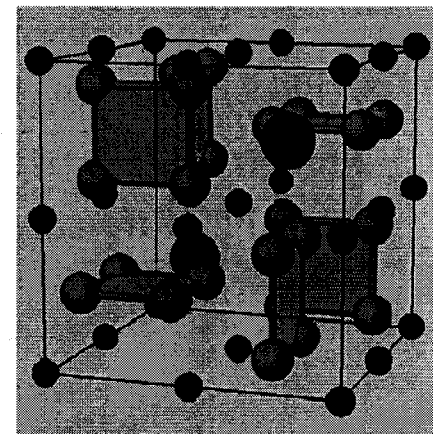
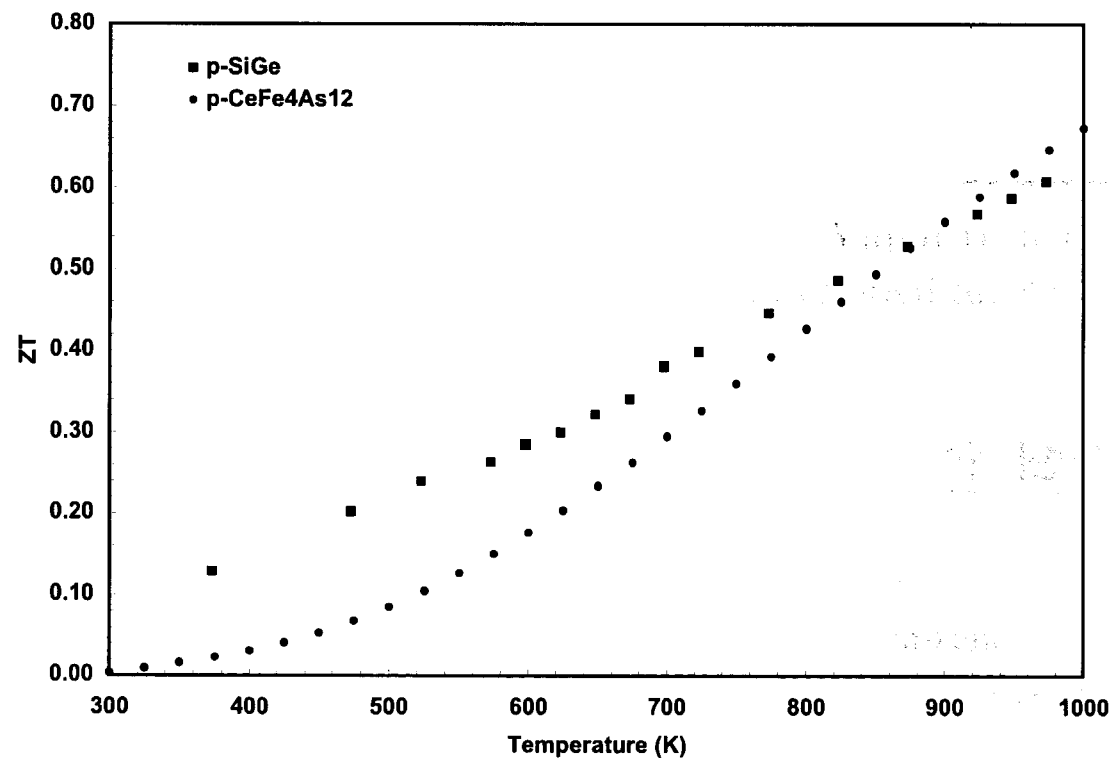




High Temperature Materials



- P-type $\text{CeFe}_4\text{As}_{12}$
 - Filled skutterudite composition synthesized in a two-zone furnace
 - Achieved $\text{ZT} \sim 0.7$ at 975K ; comparable to SiGe



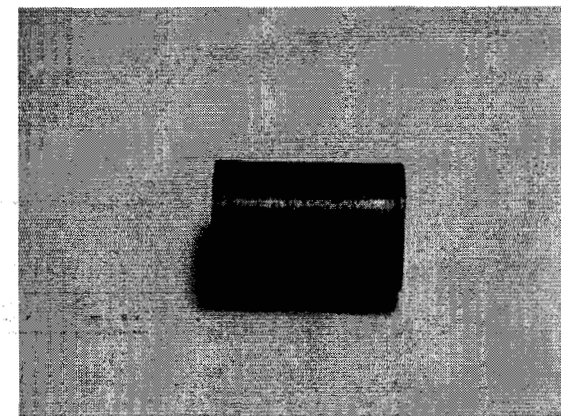
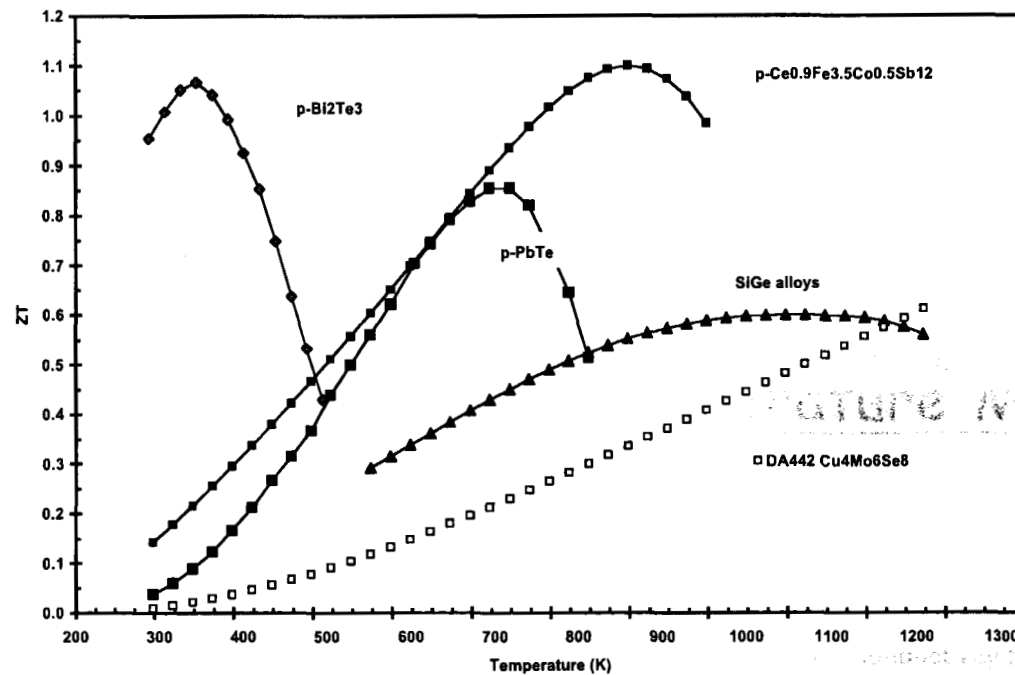
Skutterudite crystal structure



High Temperature Materials

- **Chevrel chalcogenides (Mo_6Se_8 -based)**

- Synthesized several additional Cu and Fe filled Mo_6Se_8 compositions using a powder metallurgy technique
- Measured Seebeck coefficient, electrical resistivity, and thermal conductivity from 300K to 1275K
- Achieved $ZT \sim 0.6$ at 1275K for $\text{Cu}_4\text{Mo}_6\text{Se}_8$ composition, comparable to SiGe
- Tested $\text{Cu}_4\text{Mo}_6\text{Se}_8$ sample under electrical load (potential Cu electromigration)
 - Sample shows no indication of electromigration after 6 days at 900°C under 5A load current



CuMo₆Se₈ sample tested for 6 days at 900C under 5A load